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INFLUENCE OF OCCLUDED HYDROGEN ON THE ELECTRICAL RESISTANCE OF PALLADIUM.

By W. E. McElfresh.

Presented by E. H. Hall, June 17, 1903. Received November 13, 1903.

It was observed by Graham,* in 1869, and later by Dewar,† Knott,‡ and others, that the electrical resistance of a palladium wire is much greater when the wire is charged with hydrogen than when it is in its normal state.

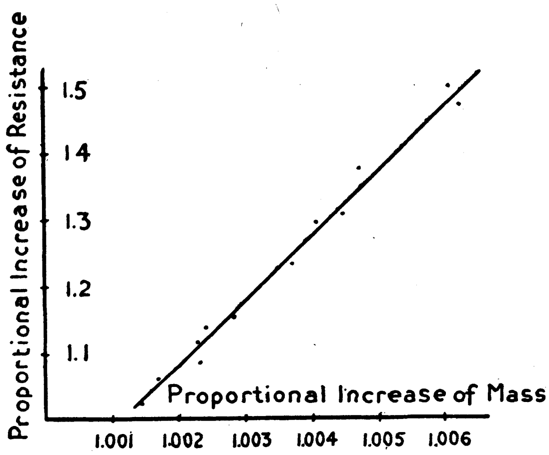

Figure 1.

Knott made a quantitative study of the phenomenon, charging a wire step by step and measuring its resistance after each charging. The curve plotted from these results is reproduced here (Fig. 1) and challenges attention immediately in regard to one or two particulars. For it is practically a straight line for all points between 175 volumes absorbed (0.0014 increase in mass of wire) and saturation (nearly 900 volumes absorbed), but this line does not point toward the origin. The resistance was first measured with no hydrogen in the wire, then with about 175 volumes, then with still greater amounts. No observations were taken to obtain points on the curve between the origin and that for 175 volumes, but, if the results as plotted are correct, it is evident that the curve, as it approaches the origin, must either bend very sharply toward the left or else it must drop below the horizontal axis. In other words, it would appear from the curve that a small quantity of occluded hydrogen, say 50 volumes, would change the resistance of the wire very slightly or, possibly, make it actually smaller than when there is no hydrogen in the wire. Knott comments on the peculiar shape of the curve, but offers no explanation, and there appears to be no record of any later attempt to repeat the experiment or to seek for a more accurate method of studying the phenomenon. The work outlined in this paper was undertaken in the hope of making a more careful determination of the curve given by Knott and, more particularly, with a view to studying its form near the origin.

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* Poggendorff's Annalen, 136 (1869).

† Trans. Roy. Soc. Edin., Vol. 27.

‡ Proc. Roy. Soc. Edin., Vol. 12 (1882-1883).

The method, employed by Knott and others, of determining the amount of hydrogen occluded — by measuring the increase in weight of the wire — appears to be incapable of giving very exact results. Accordingly, in the work described below, the wire is charged with hydrogen by being made the negative electrode of a gas voltameter and the amount absorbed is determined as follows. The electrolysing current is accurately measured at regular intervals during the charging process and the total quantity of hydrogen liberated from the electrolyte is thus easily calculated; the hydrogen which escapes from the wire is carefully collected, and its volume measured, and this volume being subtracted from the total volume liberated by the current it is assumed that the difference represents the volume of hydrogen occluded by the wire.

In the earlier experiments the voltameter was simply a glass jar of about three liters' capacity filled with a two per cent solution of sulphuric acid; a light hard-rubber frame held in place the two electrodes, the palladium wire being coiled in a slender spiral in the middle of the jar, while a platinum wire, coiled around the inner wall of the jar, formed the positive electrode; a burette with an inverted funnel fused to its lower end served to collect and measure the escaping hydrogen. Two objections to this form of apparatus at once suggested themselves. In the first place it was found that even a large funnel would not catch all of the rising hydrogen bubbles, especially toward the end of the experiment. At this time, when the wire is nearly saturated, the hydrogen escapes as a milky cloud of very small bubbles, many of which stream around beneath the edge of the funnel and so escape to the open air. In the second place, hydrogen is slightly soluble in the electrolyte, and where a large quantity of the latter is used the amount of hydrogen dissolved may be great enough to introduce a considerable error. For, by this method, the computed value of the quantity of hydrogen absorbed by the wire will include both that actually absorbed and also that dissolved by the electrolyte.

In order to overcome these difficulties, the final experiments employed a voltameter whose capacity was only about 475 cubic centimeters, and in which the palladium wire was surrounded by walls of filter paper so arranged that the liberated hydrogen could not escape otherwise than into the burette.

The accompanying diagrams illustrate the construction of the apparatus. The voltameter is made by clamping quarter-inch glass plates, *bb*, in Fig. 2, to a rectangular frame, *aa*, of hard-rubber, a thin strip of pure-gum rubber sheeting serving as packing. As thus constructed, the voltameter is slightly more than one foot in depth, while its cross-section measurements are shown in Fig. 2, which is one-half of actual size. The increased width in the middle portion of the interior allows the electrical lines of flow to be uniformly distributed around the circumference of the palladium wire, which will thus be charged evenly from all sides. The bevelled glass plates, *cccc*, fit loosely in narrow recesses provided for them in the hard-rubber frame, *aa*. Their purpose is solely to diminish the volume of electrolyte used. Fig. 3 — one-fourth of actual size — shows the same piece of apparatus in elevation, and Fig. 4 shows a cross-section at a level just below that of the lower end of the burette. The platinum wires, *dd*, parallel to the palladium wire, form the positive electrode of the voltameter. In the process of charging, the current, for a time, is sent *in* at the tops of the platinum wires and *out*

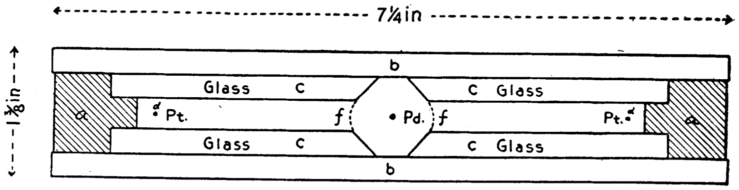

FIGURE 2.

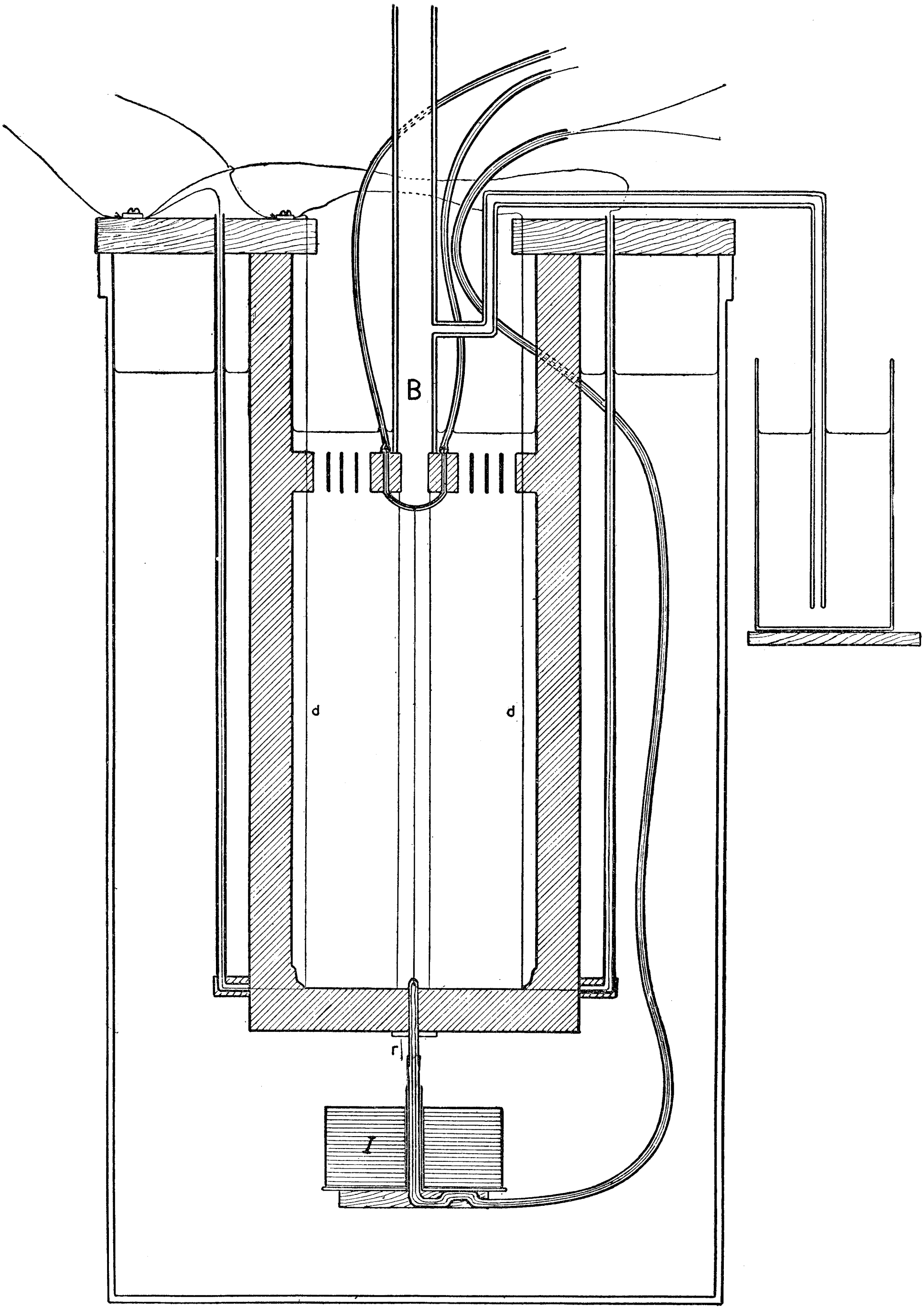

FIGURE 3.

at the bottom of the palladium; then by a throw of a commutator key it is sent *in* at the lower ends of the platinum wires and *out* at the top of the palladium. This should insure an even distribution of the hydrogen throughout the length of the wire. Two filter-paper partitions, *ff*, in Fig. 2, are introduced, one on either side of the palladium, and are held in position by having their edges caught between the glass plates *b* and *c*. These filter-paper partitions serve to prevent any possible mixing of oxygen with the hydrogen and at the same time force all of the liberated hydrogen that is not absorbed by the palladium to rise into the burette, *B*, where its volume may be measured.

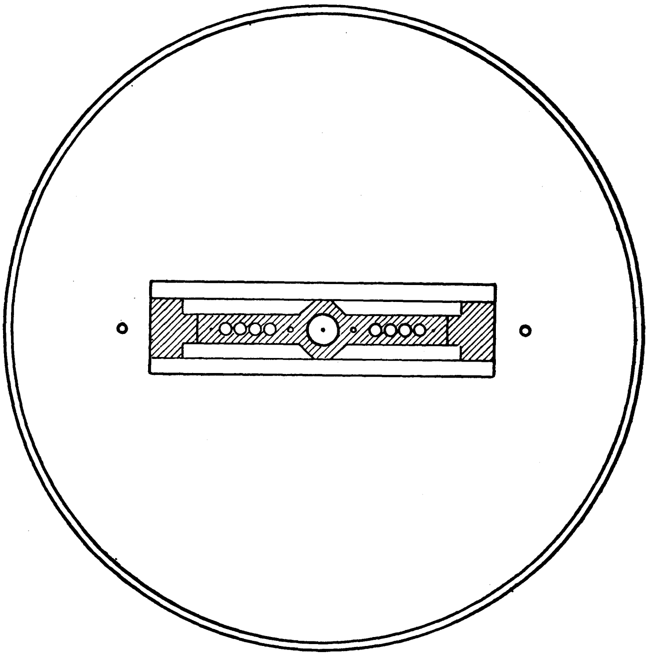

FIGURE 4.

In order to measure the resistance of the palladium wire without removing it from the voltameter it is necessary that two insulated lead-wires be permanently connected with each end. Accordingly (see Fig. 5), the upper end of the palladium wire is soldered to the middle of a copper wire whose ends are carried through small holes in the hard-rubber crosspiece and thence to outside connections. This copper wire is very carefully protected from the electrolyte by means of a special acid-proof cement which covers the submerged portion of the copper wire and the soldered end of the palladium. The two branches of the copper wire are further protected by soft-rubber tubing ("pure-gum"), which forms a water-tight jacket, its lower ends being closed with cement. To the lower end of the palladium wire are soldered two long copper wires which lead to outside connections. Incasing one of these wires in a rubber tube of very small bore serves to insulate them from each other; a rubber tube of larger bore contains the pair of wires, thus insulated from one another, and protects them from contact with the water in the outer jar. The palladium wire increases in length as it absorbs hydrogen, and must be subjected to a considerable tension if it is to be kept straight. To this end a glass tube, about two inches long, is drawn over the lower lead-wires until it encloses the lower end of the palladium; the upper end of this tube is filled with cement; and over its lower end is drawn the larger rubber tube mentioned above. In this way a water-tight jacket is provided for the lead-wires, from the soldered junction to the outside connections, and no metal, excepting the platinum and palladium electrodes, is anywhere exposed to the electrolyte. The glass tube passes through a hole in the bottom of the hard-rubber frame, and a soft-rubber washer cemented to the latter allows freedom of motion to the tube and at the same time prevents escape of electrolyte. This washer is shown as *r* in Fig. 3. A heavy iron weight, *I*, is attached to the rubber-incased lead-wires, and serves to keep the palladium wire straight as its length increases under the charging process.

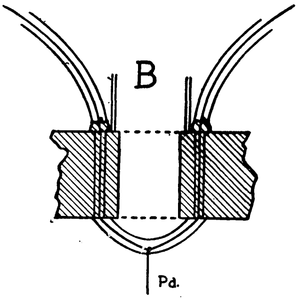

FIGURE 5.

In order that the electrolyte may easily be kept at a constant level in the voltameter, a branch tube in the side of the burette, near its lower end, leads outward, and finally dips into a larger jar of the electrolyte placed near the voltameter. This jar is shown on a small scale in Fig. 3. When the burette is filled with electrolyte this branch tube also fills, and thereafter the level of the electrolyte in the voltameter may be adjusted by raising or lowering this outer vessel.

The voltameter, with the iron weight hanging below it, is suspended in a glass jar of about 40 liters' capacity, filled with water. This water bath serves to prevent sudden changes of temperature, while a mechanical stirrer, operated continuously by an electric motor, insures a uniform temperature throughout the apparatus and so eliminates disturbing thermo-electric currents.

The method of measuring the resistance of the palladium wire is shown in Fig. 6.

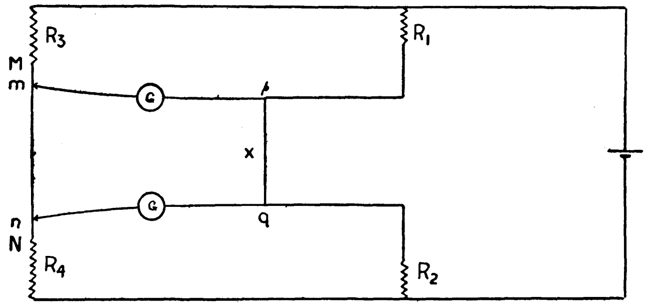

FIGURE 6.

In this diagram, x is the palladium wire, and MN is the wire of a cylindrical rheostat (a Wheatstone-Kirchhoff bridge), while m and n are points on this wire whose potentials are equal respectively to those of the points p and q. If V is the total resistance of the wire MN, and if v is the resistance of the portion included between m and n, then

$$x = \frac{v\,(R_1 + R_2)}{R_3 + R_4 + V - v}.$$

R_3 and R_4 were each equal to about 300 ohms, while R_1 and R_2 were 5-ohm coils. The various resistances were kept at constant temperature (within one degree), and reversals of direction of current flow should have eliminated any errors due to thermo-electric effects. The resistance of the palladium wire was in the neighborhood of 0.1 of an ohm, and the method of measuring gave results which agreed amongst themselves to within one-tenth of one per cent.

The charging current was between 0.02 and 0.03 of an ampere, and was measured by a shunted ammeter which gave readings to within a hundred-thousandth of an ampere. The value of the current strength was needed solely for the purpose of calculating the volume of hydrogen liberated in a given length of time, and therefore it seemed best to calibrate the ammeter by actually measuring the volume of hydrogen liberated per minute under the conditions of the experiment. Accordingly, at the close of one of the regular experiments as described below, the charging current was allowed to continue for a number of hours (twelve in one case, thirty in another) after the wire had apparently reached a state of saturation. At the end of this time, the palladium being unquestionably saturated, the volume of hydrogen liberated per minute was carefully measured and compared with the average ammeter reading. Two independent trials of this sort gave 6.973 and 6.975 cu. cm. as the volume (reduced to 0°C. and 760 mm. pressure) set free per minute by one ampere of current — as measured by the ammeter employed in this work.

In the final experiment the method of procedure was as follows. A length of palladium wire, freshly cut from the original coil, was cleaned by washing in caustic potash and then in distilled water. It was annealed by bringing it to a white heat in the open air and allowing it to cool quickly, the heating being accomplished by passing a current of electricity through it. This process left no visible tarnish, though the surface of the wire appeared less lustrous than before heating.* After the annealing the palladium was mounted in the voltameter, as already explained, and the latter was placed in its water bath, and this was stirred continuously. This bath was, approximately, at the room temperature, and by keeping the latter fairly constant the temperature of the water bath did not change during the progress of the experiment by more than 1°C. The resistance of the wire was then carefully measured. In this work, the commutator, M, in Fig. 7, was set so that the circuit of the charging battery, B_1, was broken, while the current from another battery, B_2, was allowed to flow through the palladium wire and the resistances R_1, R_2, R_3, R_4, etc. The wheel rheostat was included between R_3 and R_4, and on this rheostat were found balancing points (see Fig. 6) for the two ends of the palladium wire, i. e., points so situated that when one of them was connected, through a sensitive galvanometer, with the appropriate end of the palladium wire, no deflection was observed. To guard against any errors from thermo-electric effects, these balancing points were located four times in each measurement of resistance, the commutator N (in Fig. 7) being used to reverse the current through all the resistances, while, for each position of N, reversal of the commutator M, by turning it through 90°, had the effect of turning the palladium wire end for end with respect to the remainder of the circuit.

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* In a preliminary experiment a piece of palladium cut from the same coil had been annealed in an atmosphere of nitrogen, with the result that the wire retained its high polish, but refused, when exposed to the nascent hydrogen, to absorb the latter in any considerable quantity.

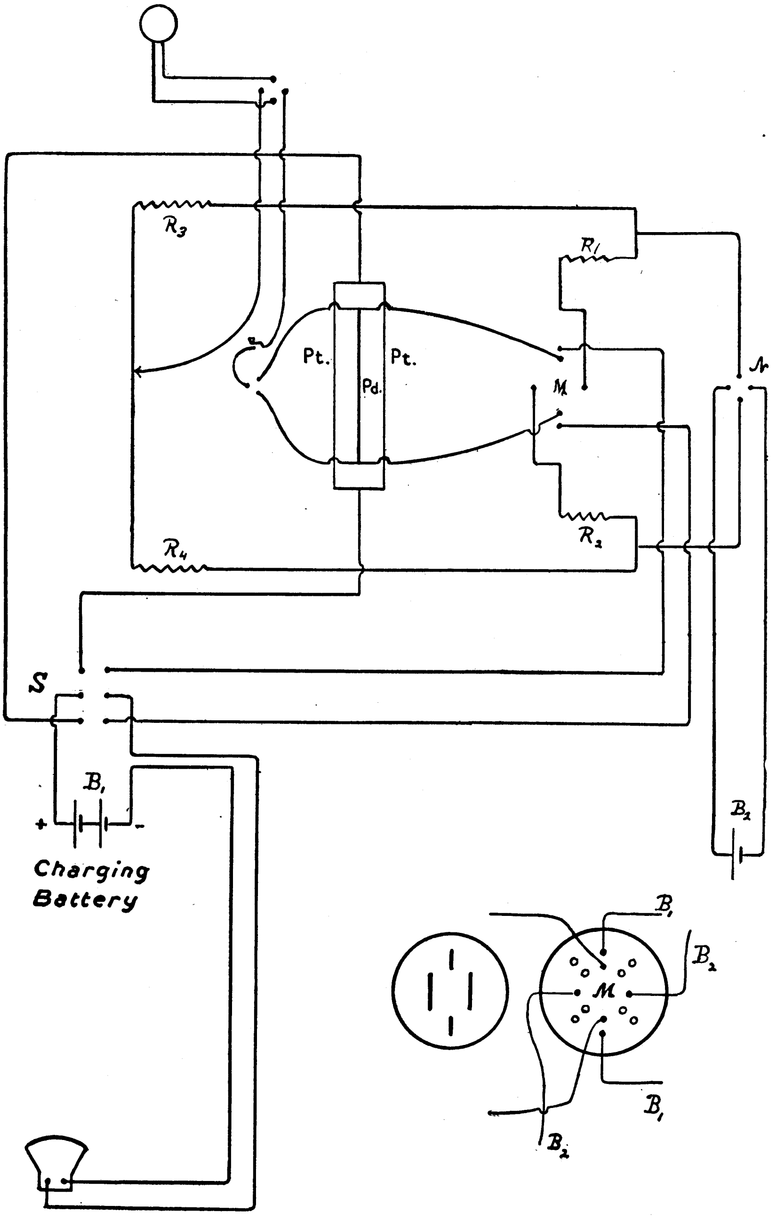

FIGURE 7.

By turning the commutator M through 45°, after the measurement of resistance before charging, the resistance measuring circuit was broken and the charging current from B_1 was started. This was allowed to flow for a carefully measured length of time, — fifteen minutes, — and ammeter readings were taken at the end of every minute. A turn of the commutator key, M, stopped the charging current, and at the same time made the proper connections for measuring resistance; but before the latter work was undertaken the burette was examined with a view to recording the volume of hydrogen collected. No hydrogen was found in the burette after this or any other of the earlier chargings; and it was therefore assumed, in such cases, that the total volume liberated during the charging run, as calculated from ammeter readings, had been absorbed by the wire. This was usually, for each fifteen minutes' run, about twenty times the volume of the wire. The resistance of the wire, thus charged, was then carefully measured as before, just fifteen minutes being allowed for this work. Again the wire was charged with an additional twenty volumes (approximately) and its new resistance immediately determined. This process, of alternately charging the wire and measuring its resistance, was continued until the wire appeared to be saturated, the entire experiment requiring about thirty hours of uninterrupted observations. This slow charging rate was employed because preliminary experiments had shown that time is a very important element in the absorption of hydrogen by palladium; if a strong current is used, most of the liberated hydrogen bubbles up to the surface of the liquid, even at the beginning of the run with a fresh wire. But with the weak currents used in these experiments no hydrogen bubbles were seen until after the palladium had absorbed more than six hundred volumes (75 to 80 cu. cm.); oxygen bubbles, of course, rose from the platinum wires from the very start. The first appearance of hydrogen in the burette was carefully watched for, and thereafter, at the close of each charging run, the volume of hydrogen in the burette was carefully recorded and reduced to standard conditions of pressure and temperature. In the subsequent calculations the new volume of hydrogen, collected in the burette during each charging period, was substracted from the total volume liberated by the current during that period, as calculated from ammeter readings, and it was assumed that the difference represented the volume of hydrogen (at 0° C. and 760 mm. pressure) absorbed by the wire during that run. In the earlier part of the work the charging time was, in each case, just fifteen minutes; later, when the hydrogen was escaping very freely, this time was lengthened. In every case just fifteen minutes was allowed, between two consecutive chargings, for measuring resistance. While the charging current was flowing, ammeter readings were taken at intervals of one minute.

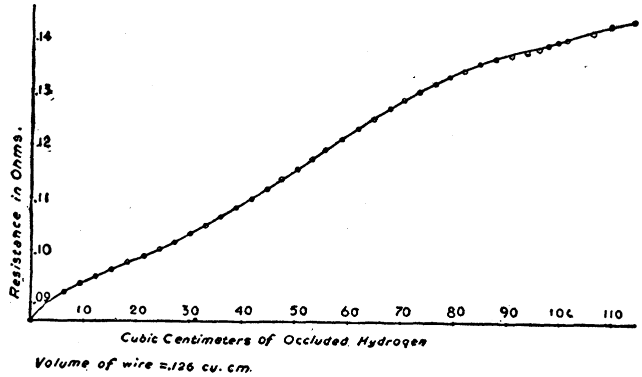

Figure 8.

Figure 8 and Figure 9 show the results of two independent trials. Although three months intervened between these trials, the condi-

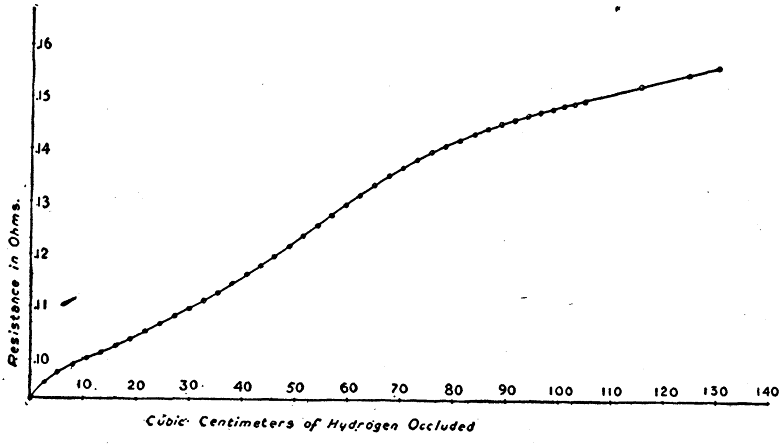

Figure 9.

tions of the second were made as nearly as possible like those of the first. The palladium wires were cut from the same piece and were subjected to practically the same treatment in preparation for their respective experiments. The curves are plotted with increase of resistance (above the resistance at start) for ordinates, and cubic centimeters of hydrogen occluded for abscissae. These curves should, then, be similar in form to curves whose coördinates are "proportional increase of resistance" and "proportional increase of mass" (see Fig. 1). The curves exhibited here show a decided increase in the resistance of the palladium from the very beginning of the experiment. In fact the first few volumes of occluded hydrogen seem to be more effective, in increasing resistance, than similar quantities added later in the charging process. The two curves are noticeably similar, and show a marked departure from the straight line. The writer hopes to repeat these experiments, varying the conditions somewhat, as regards rapidity of charging, temperature, etc., and, perhaps, using apparatus of different design, in the hope of fixing, more conclusively, the exact shape of the curve.

The maximum quantity of hydrogen occluded is, in the case illustrated by Fig. 8, 130 cu.cm. or about 1030 volumes. This increases the resistance from 0.0927 ohm to 0.1558 ohm, an advance of 68 per cent. It is believed that the last point of this curve corresponds, practically, to saturation of the wire; after the data for this point had been taken, the charging current was allowed to continue for twelve hours, and the resistance was measured at the end of the first five hours and again at the end of the twelve hours, but the results were practically those obtained for the last point of the curve. No attempt was made to measure the volumes of escaping hydrogen during this twelve-hour run. Knott found a maximum increase of resistance of about fifty-two per cent (0.1865 ohm to 0.285 ohm), corresponding to an occlusion of from 900 to 1000 volumes. Graham, in Poggendorff's Annalen for 1869, states that the conductivities of pure palladium and the hydrogen-charged palladium are as 5.99 to 8.10. He does not state the exact quantity of gas occluded in the hydrogen-charged wire, but elsewhere in the same paper describes experiments in which 900 volumes were absorbed.

The method employed in these experiments seems to be capable of results more accurate than those obtained by the investigators named above, and these results would seem to indicate that the resistance of the palladium wire, as hydrogen is absorbed, increases rapidly from the very start; it also appears that the increase of resistance is not strictly proportional to the volume of hydrogen occluded.

Grateful acknowledgment is made of many valuable suggestions and much assistance received from Professor E. H. Hall, of Harvard College.

Jefferson Physical Laboratory, Harvard
University, May, 1903.